Optical Characterization of Length Sorted Single Wall Carbon Nanotubes

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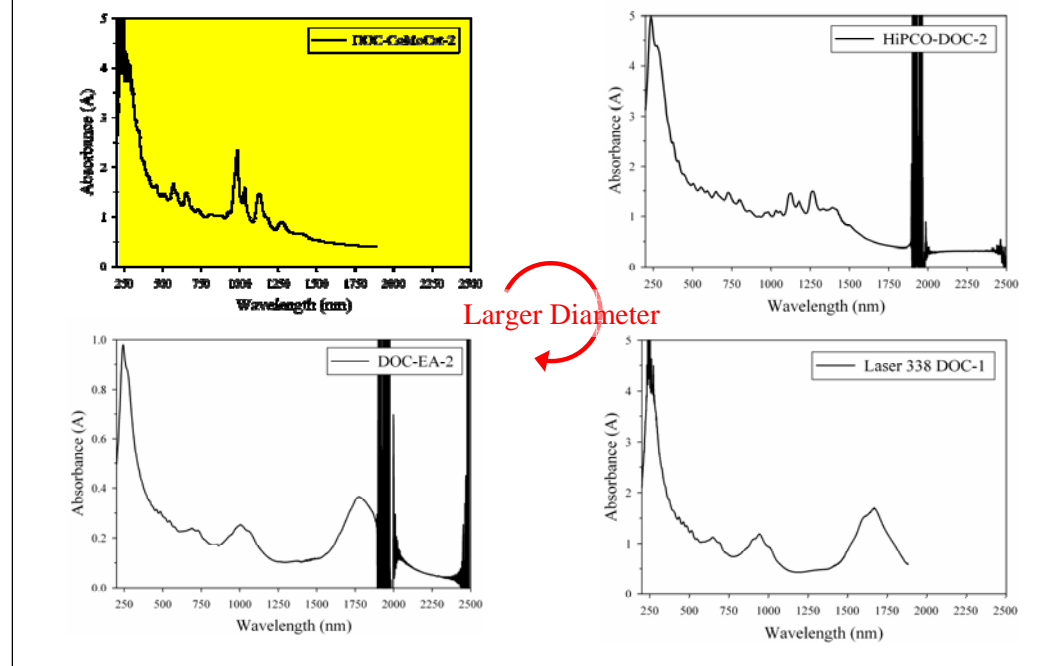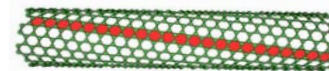National Institute of Standards and Technology
Gaithersburg, MD

Dr. Jeffrey Fagan's presentation from the 3rd NASA-NIST Workshop on Nanotube Measurements held Sept. 26th – Sept. 28th 2007 in Gaithersburg, MD.

Carbon Nanotubes:

In this presentation results found using Cobalt-Molybdenum-Catalyst (CoMoCat) type tubes (such as in the upper left corner) are primarily presented. However, for each result we have worked with a number of single wall carbon nanotube (SWCNT) sources, including CoMoCat, high pressure CO (HiPCO), Laser, and Electric Arc materials, and found the results to be independent of the SWCNT type used, or consistent with known property variation with diameter. On this slide Absorption spectra of each of these sources are shown for comparison, having been prepared by an identical procedure of tip sonicating 1 mg /mL of SWCNT powder in 2 % (mass / volume) sodium deoxycholate (DOC) solution followed by centrifugation at 21 000 x g (where g is the acceleration due to gravity) for 2 h. The spectra shown are for the resulting supernatant, and the contributions of the DOC and the quartz cuvette have been removed. Noise in the spectra between 1880 nm and 2100 nm is due to the strong absorption of water within this range.

2

Surfactant Choice:
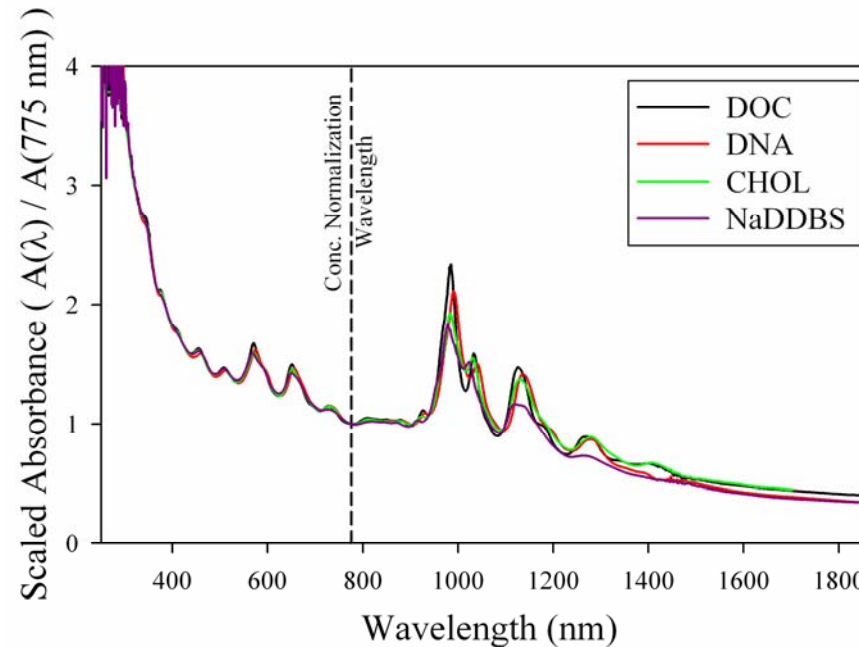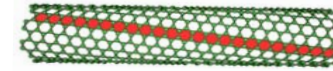
Results here are also shown either for DNA dispersion, or dispersion by sodium deoxycholate (a bile salt surfactant). Due to differences in the quality of individualization generated by different surfactants, we identically prepared fours samples from a common batch of material to evaluate the relative quality of the achieved dispersions. Normalized for concentration differences at 775 nm, it is clear that deoxycholate and (GT)15 DNA yield larger peak intensities, indicative of better SWCNT individualization, than the commonly used sodium cholate or sodium dodecyl-benzyl-sulfate. Sodium dodecyl sulfate was also evaluated and performs more poorly than sodium dodecyl benzene sulfate (NaDDBS). This particular sample is weighted to the (6,5) SWCNT, but also contains significant percentages of (7,5) and (7,6) SWCNTs among others.

Surfactant Choice:
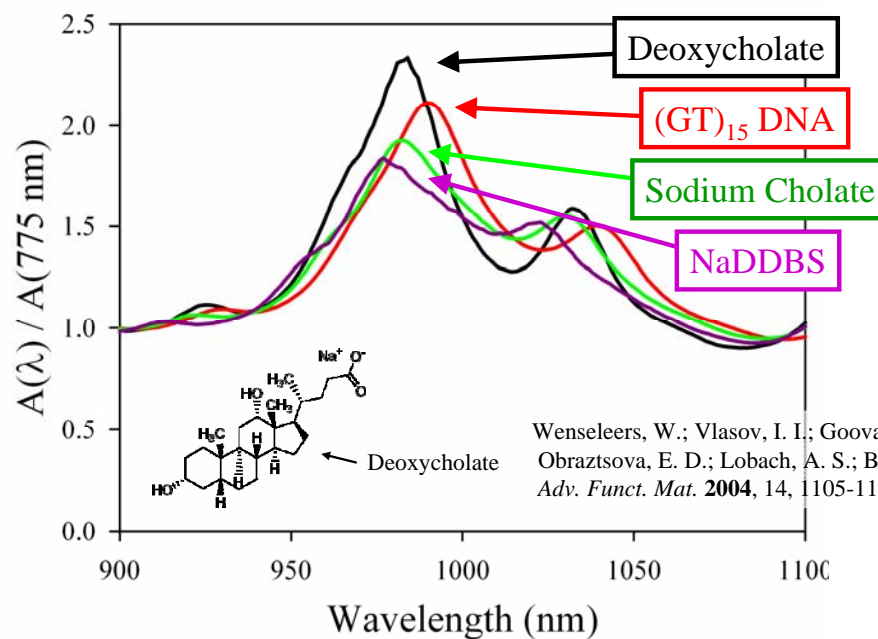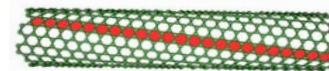
The difference in peak intensity is most apparent in the E11 optical transitions. It can be clearly seen in this figure that the DOC and (GT)15 DNA yield the most intense and narrow features, indicating the best individualization. One or the other of these two surfactants were used for all of the remaining work presented in this talk. It should be noted that DOC was initially shown to be an excellent surfactant by Wenseleers et al. [*Adv. Funct. Mat.* **2004**, 14, 1105-1112], and has been further shown to be an excellent surfactant by Haggenmueller et al. [*submitted to Langmuir* **2007**].
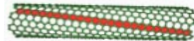
Why Length Sort?:
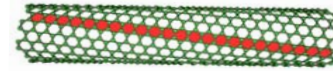
The length of the nanotube is its most obvious and second most important characteristic!

Tube length affects the optical properties, percolation lengths for electrical, thermal and mechanical properties, alignability processing variables such as viscosity, and the toxicity of the nanotubes.

Short

Long
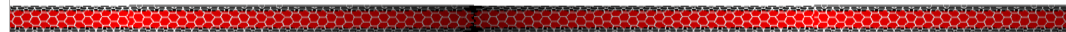
Why length sort? The length of the nanotube is extraordinarily important in dictating the expected properties of the material, as well as its processability. We have found that the length directly impacts the key optical and electrical properties of the SWCNTs, as well as other factors such as the cellular uptake rates of the dispersed nanoparticles. Since many properties are directly affected by length it is important to perform the separation such that these effects can be measured.

Separating Carbon Nanotubes:

Several techniques have been used to sort nanotubes by tube length.
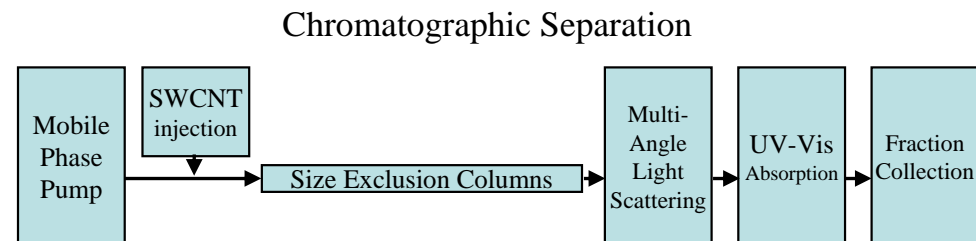
Method Comparison

M. Zheng et al. at Dupont

Fagan et al. at NIST

Method	Analytical Preparative	Batch Size	On-Line Analysis	Fraction / DI Mw / Mn	SWNT size (nm)	Comments
SEC	A + P	200 (2000) µg	Photodiode array, MALS, Viscosity, Refractive Index	1.5 to 1.1	50 to 500	Best on-line measurements. Short SWNTS contaminated with long. DNA dispersions only. Not robust.
FFF	A	20 µg			20 to >1000	Analytical only. Best separations. Many dispersion types. Robust.
UC	P	20000 µg	none	< 1.5	20 to >2000	Large quantities. Many dispersion types. Broad size range. Very Robust.
SWNT fracture	P	> 10000 µg	none	> 1.5	50 to 1000	Very broad distributions. Damaged SWNTs. Large quantities. Many dispersion types. Can only shorten.
Gel EP	A	< 20 µg	none			Very small quantities. Only certain dispersions

Several techniques have been proposed/developed for length separation of SWCNTs, however none has been commercialized due to either the extremely high cost (> ≈ $50 / mg for SEC), unsuitable methodology for scale-up, or the poor performance of the separation. For the purposes of this talk, size exclusion chromatography, developed by Ming Zheng and others at DuPont, and using DNA dispersed SWCNTs, and ultracentrifugation length separation, developed at NIST and using deoxycholate dispersed SWCNTs, are of primary interest.

Size Exclusion Chromatography:

The first technique that we used to separate the nanotubes by length was size exclusion chromatography (SEC). In SEC a plug of nanotube solution is injected into a column containing porous packing with various size pores, into which the SWCNTs will fractionate based upon the size of the nanotube. As the solution moves through the column smaller tubes spend progressively more time within these pore volumes, hence longer SWCNTs move faster through the column, and elute earlier. For DNA wrapped SWCNTs, this procedure was developed by Zheng *et al.* at DuPont [Huang, X. Y.; McLean, R. S.; Zheng, M. *Anal. Chem.* **2005**, *77*, 6225., Zheng, M.; Jagota, A.; Semke, E.D.; Diner, B.A.; McLean, R.S.; Lustig, S.R.; Richardson,R.E.; Tassi, N.G. *Nat. Mater.* **2003**, *2*, 338.].

  In our setup Dr. Barry Bauer added online multi-angle light scattering and UV-Vis absorption detection before the fraction collector to improve the analytical measurement. All of our SEC results are contained in a recent JACS article [Fagan, J. A.; Simpson, J. R.; Bauer, B. J.; Lacerda, S.; Becker, M. L.; Migler, K. B.; Hight Walker, A. R.; Hobbie, E. K. *J. AM. CHEM. SOC.* **2007**, 129, 10607-10612], Results and details of the online light scattering characterization are submitted to *J. Phys Chem C.* [Bauer, B.J.; Fagan, J.A.; Hobbie, E.K.; Chun,J.; Bajpai, V. *submitted to J. Phys. Chem. C.* **2007**.].

Size Exclusion Chromatography:
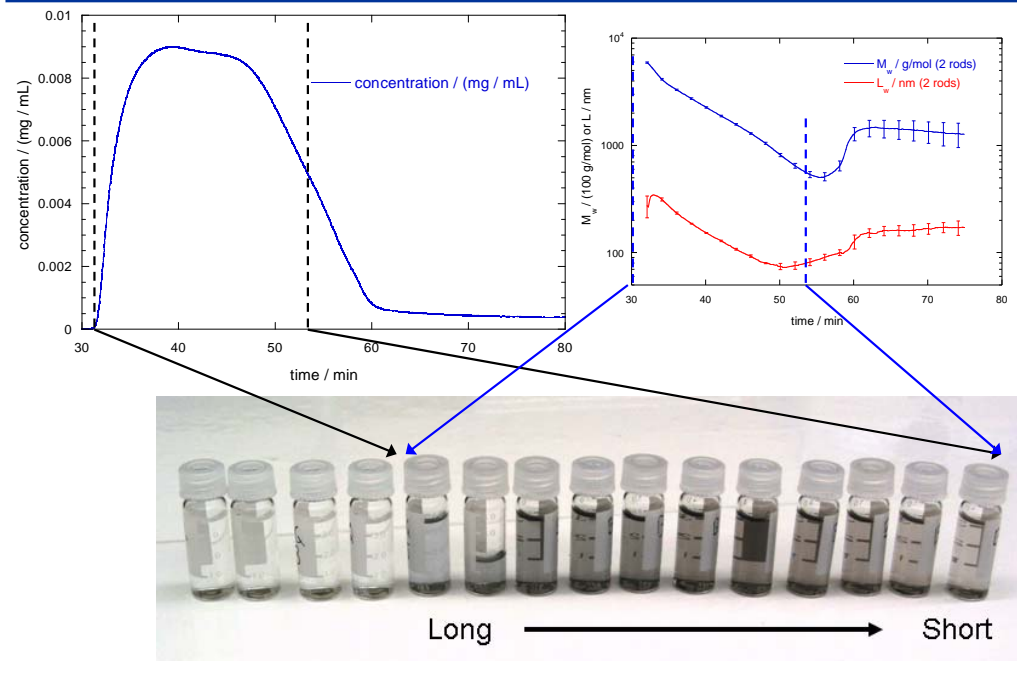
A set of fractions from the SEC separation is shown. The longest SWCNTs begin eluting in our fifth fraction, indicating the exclusion limit of the column, and get progressively shorter through fraction 15, at which point DNA begins to elute and the SWCNT concentration drops sharply. The multi-angle light scattering size fit as a function of fraction number is shown on the right side.

Size Exclusion Chromatography:

AFM Image

Fraction 6 SEC sorted
ssDNA – SWCNTs on MICA

Legend:
- ○ MALS (Rod fit)
- ■ DLS
- ◆ AFM
- — Exponential Fit
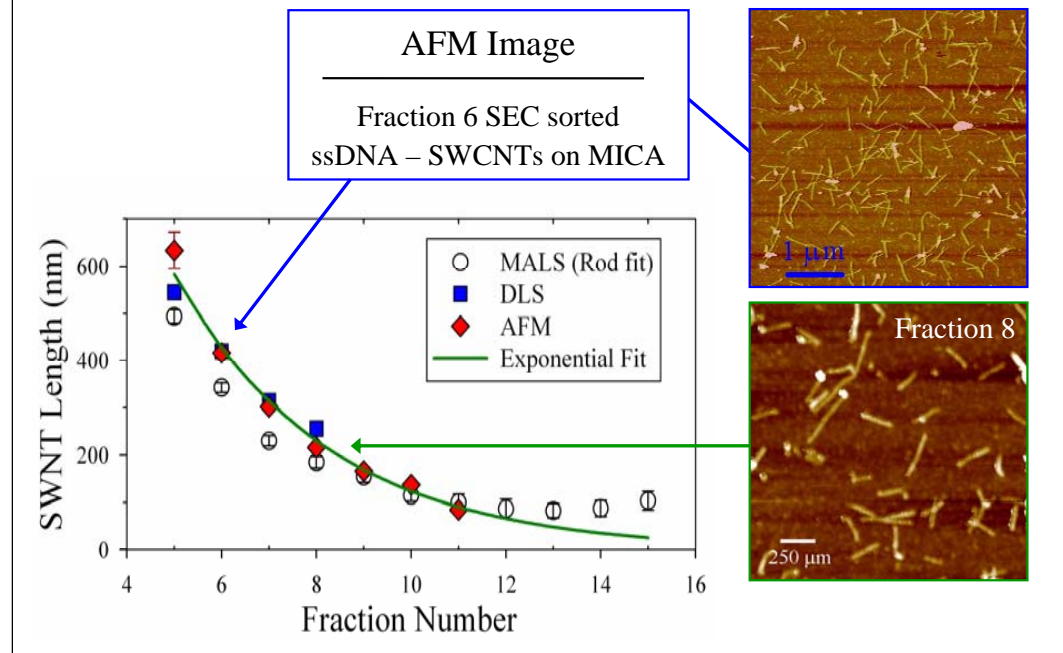
Fraction 8

The average length of each fraction was measured by a few different techniques. Atomic force microscopy (AFM) images from two of the fractions are shown to the right. The vast majority of SWCNTs imaged by the AFM are straight. The green line in the length versus fraction number figure is the best fit exponential (the theorectically expected form) to the AFM and dynamic light scattering (DLS) length data. More details are given in the Fagan *et al.* JACS paper and its supporting online information.

Size Sorted SWCNTs
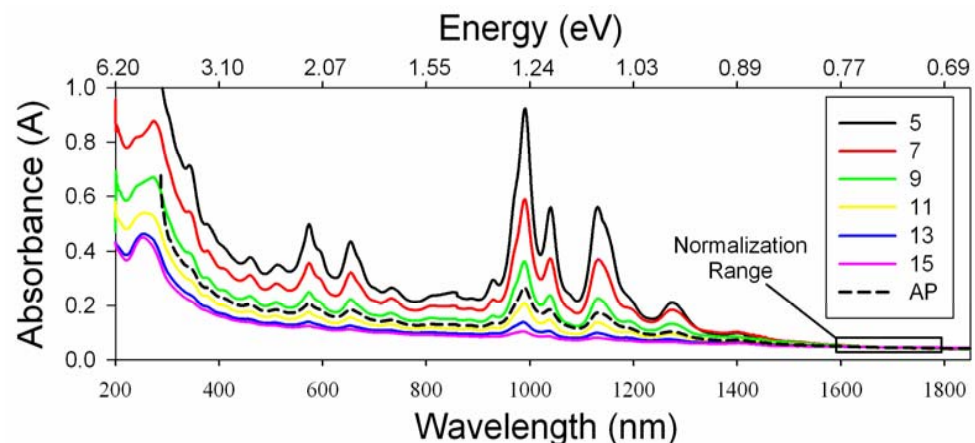
Peak absorbance / baseline absorbance *increases* with SWNT length!

Key finding for measuring SWNT purity and for applications.

Results published in Fagan et al. *JACS* **2007**, 129, 10607-10612.

A key finding in measuring the separated fractions is that the longer SWCNTs show substantially larger peak absorption relative to the baseline absorption regardless of the wavelength chosen for concentration normalization. Here the normalization is made in the long wavelength limit beyond the E11 transitions of these small diameter SWCNTs. Note also that the location of the peaks do not change with the fraction number, indicative that bundling is not occurring.
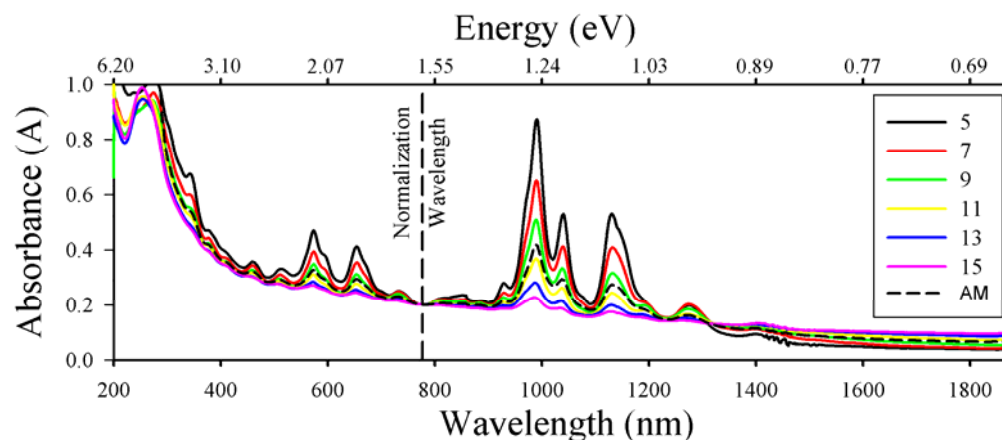
Size Sorted SWCNTs

Peak absorbance / baseline absorbance *increases* with SWNT length!

Key finding for measuring SWNT purity and for applications.

Results published in Fagan et al. *JACS* **2007**, 129, 10607-10612.

The increase in peak to baseline ratio finding is regardless of the wavelength chosen for concentration normalization. This finding can also not be explained away by purity arguments unless the injection concentration was less than 13 % pure using only the SEC results; the estimated value (backed up by SEM, TEM, and thermo-gravimetric analysis (TGA) of the raw soot and the dispersed material) is (90 to 95) % purity of SWCNTs in the injected liquid. The purity value would have to be even lower < 4 % using results measured using centrifugation sorting that will be described later in the talk. Of note is that the peak absorption in the longest fractions approaches the size of the Pi-plasmon absorption feature. Generally even the absorption spectra of the as produced (sonicated, 2 h centrifuged, labelled in this figure as AM) is substantially better than most spectra reported in the literature.

Size Sorted SWCNTs
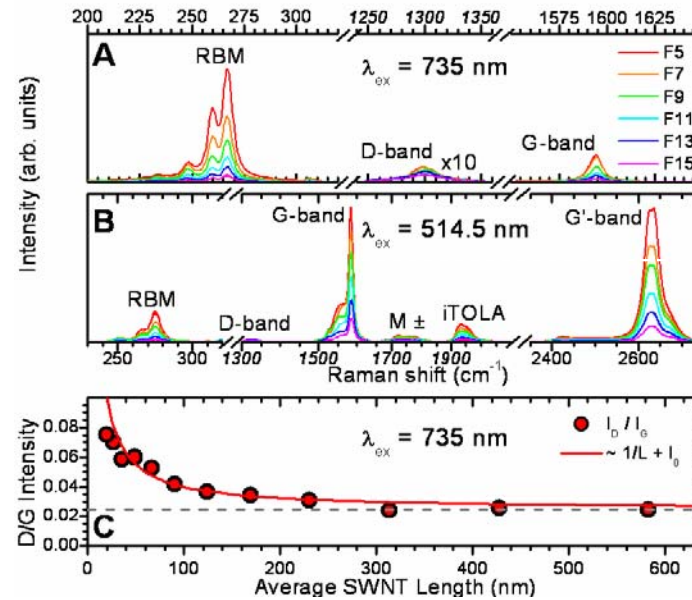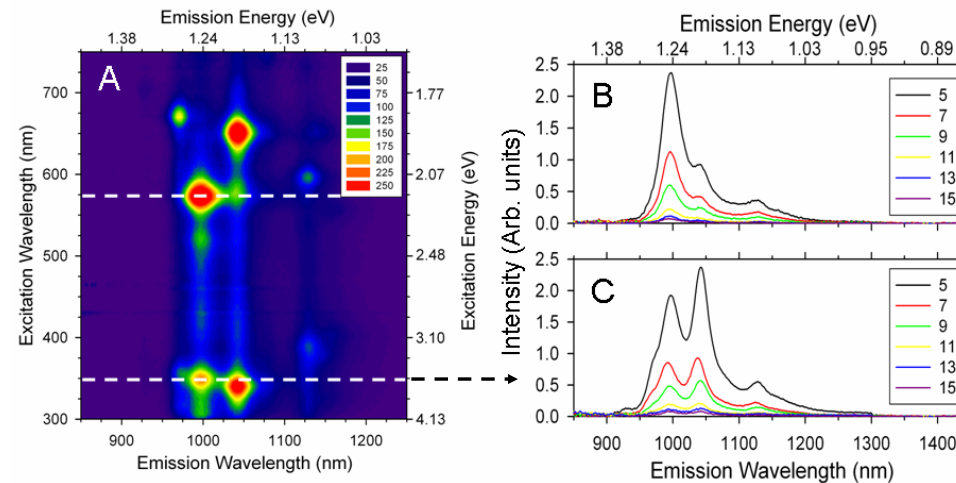

Raman intensity also *increases* with SWNT length!

The Raman intensity of the fractions also increases with the length, strongly for the RBM, G, G', iTOLA, and M modes, very weakly for the D band. Thus the D/G ratio decreases dramatically with SWCNT length to a very small value. Jeff Simpson performed these measurements, and will be presenting a poster detailing the results tonight.

Size Sorted SWCNTs

Fluorescence intensity *increases* with SWNT length!

As the peak absorbance increases with length, so does the fluorescence. Here is shown the PL map of the DNA dispersed CoMoCAt SWCNTs and slices through excitation of the (6,5) SWCNT E33 and E22 optical transitions. The solutions were diluted to a common absorbance of 0.15 / cm at 775 nm for these measurements. This dilution is meant to account for differences in concentration of the SWCNTs, and the solutions had individual absorption spectra as shown on page 11.

Size Sorted SWCNTs
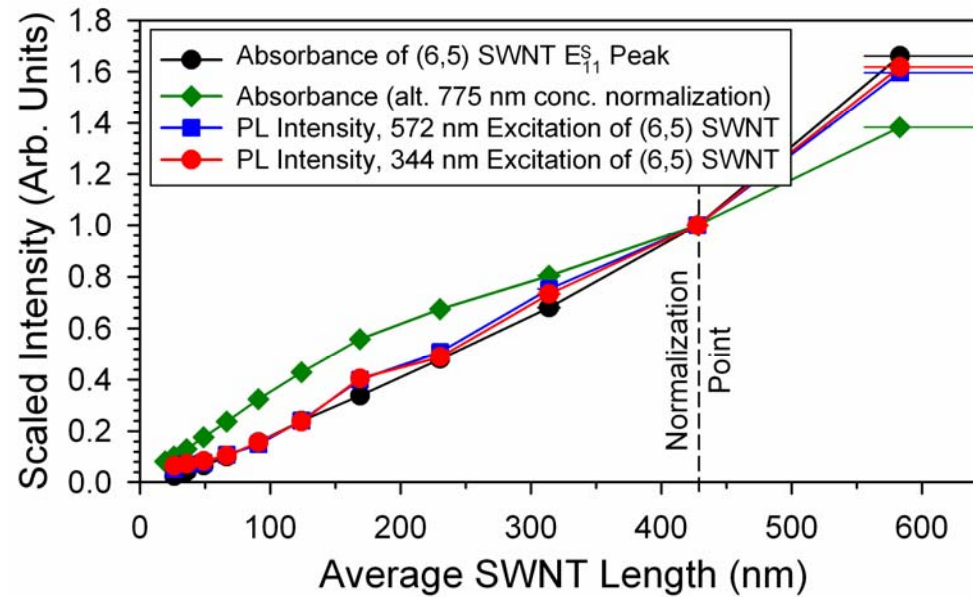
Plotting the peak absorbance (of the E11 (6,5)) and the fluorescence of the (6,5) peak due to E33 and E22 excitation, both are found to be roughly linear with the SWCNT length. The (6,5) SWCNT is shown here simply because it has the highest concentration in the dispersion, and the largest feature size, and thus the largest S/N ratio. Similar plots with other SWCNT features show the same behavior.

Changing Gears:

Okay.

Prove it is not a purity effect or an unrecognized artifact.
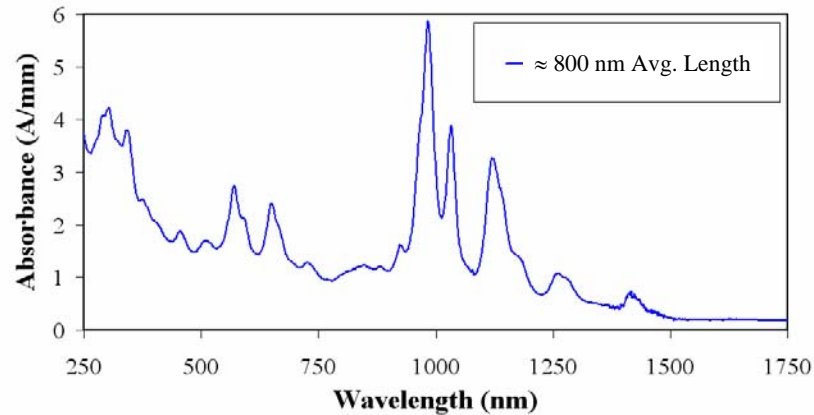
Despite all of the SEC evidence, one might ask "Are these results universal? Or are they a result of an unrecognized experimental artifact?" Using a second, independent, method of length separation we can demonstrate that the effect is real, and that even better optical properties can be achieved through length separation. The figure shows an approximately 800 nm long fraction in which the E11 peaks are larger than the Pi-plasmon absorption without any chirality separation.

Length Separation by Centrifugation

Length fractions can also be produced through centrifugation

1257 rad/s , 94 h
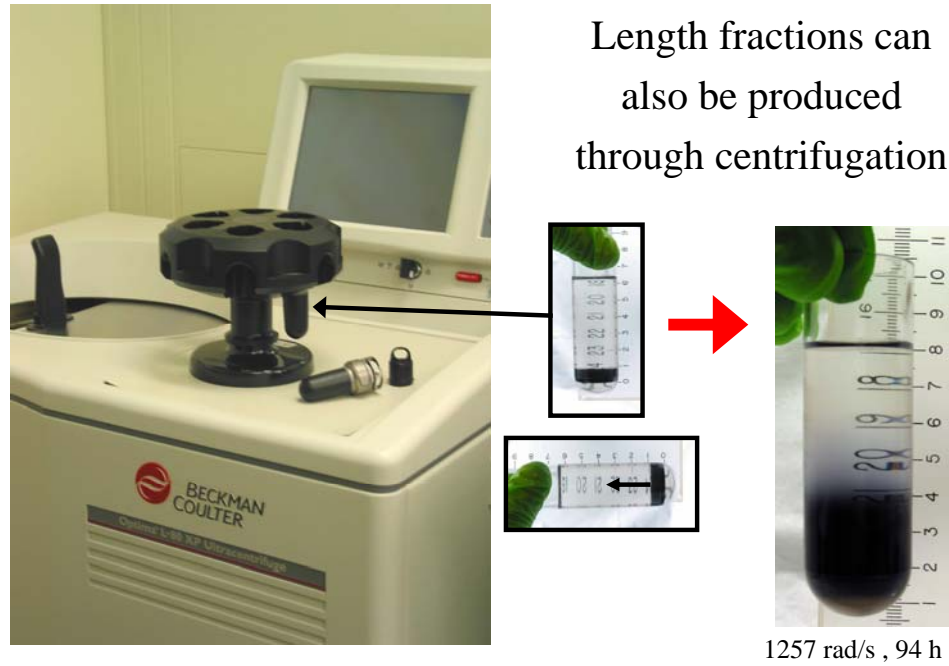
The second technique used for length fractionation in this work was performed using centrifugation of the SWCNTs in a dense liquid. Separation is driven by the difference in the transient motion of SWCNTs in a dense liquid due to a difference in scaling of the buoyancy and frictional forces with the aspect ratio of a SWCNT.

Chirality (Diameter) Separation by Centrifugation

From Arnold *et. al.* Nature Nanotechnology, 1, 60-65, 2006

Demonstrated chirality separation of SWNTs by exploiting differences in the densities in this surfactant solution.

Separation is achieved as the SWNTs go to their *equilibrium* positions, exploiting
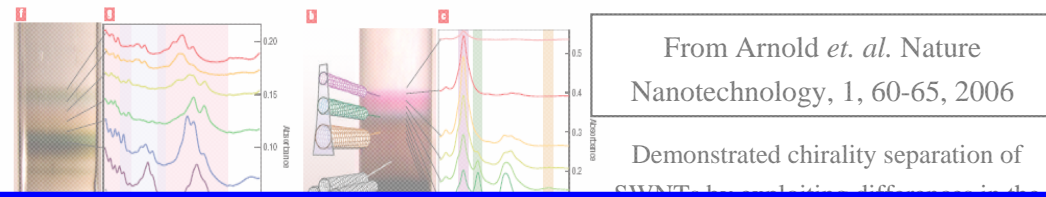
$$\Delta\rho_{SWNT} = \langle \rho_{SWNT} \rangle - \rho_{SWNT,i}$$

Question:

How fast to the SWCNTs move?

We figured this out, frankly, by incorrectly performing the chirality separation demonstrated by Arnold et al. in [*Nature Nanotechnology*, 1, 60-65, **2006**], and recognizing that we had achieved length separation instead. The key is utilizing the relative velocities of SWCNTs when the difference in buoyancy force on any given SWCNT is minimal compared to a large difference between any surfactant encapsulated SWCNT and the medium.

Length Separation by Centrifugation

The velocity of a rod in response to the centrifugation is length dependent!

Thus: By changing parameters from the Arnold et al. experiment we can alternatively exploit the length dependent velocity to fractionate SWCNTs by their length

This works best when

$$\Delta\rho = \rho_s - |\rho_{SWNT}| \gg \Delta\rho_{SWNT} = |\rho_{SWNT}| - \rho_{SWNT,i}$$

Such that the driving force for chirality separation is very small compared to for length separation

Because the velocity of a rod (in creeping flow) is length dependent, a "race" can be run and the SWCNTs separated by fractionating layers with different traveled distances.

Length Separation by Centrifugation

The flux is $N_i = \dfrac{c_i F_{buoyancy}}{f_i} - D_i \nabla c_i$ with $D_i = \dfrac{k_B T}{f_i}$ where f_i is the friction coeff.

With a buoyancy force of $F_{buoyancy} = \pi r^2 \ell * (\rho_s - \rho_{SWNT,i}) * G$

Where G is the centripetal acceleration >> 1 g

The friction coefficient depends on length differently than the buoyancy force.

4: $f_\parallel \propto \dfrac{\pi \eta \ell}{\gamma} \left(\dfrac{1 + 0.307/\gamma}{1 - 0.5/\gamma} + 0.426/\gamma^2 \right)$, $f_\perp \propto \dfrac{\pi \eta \ell}{\gamma} \left(\dfrac{1 + 0.307/\gamma}{1 + 0.5/\gamma} + 0.119/\gamma^2 \right)$, $\gamma = \ln(\ell/r)$
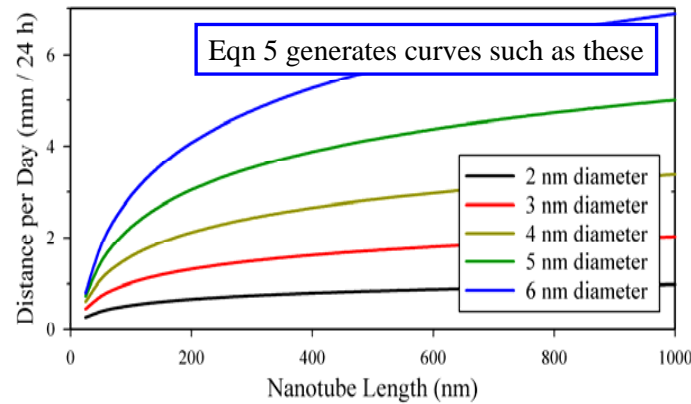
Leading to a length dependent velocity of the SWNTs, with longer tubes moving faster.

5: $N_i(\ell) \propto c_i \dfrac{(\rho_s - \rho_{SWCNT,i}) G r^2}{\eta} \dfrac{\gamma^4 + 0.614\gamma^3 + 0.3883\gamma^2 - 0.3943\gamma}{2\gamma^3 + 0.615\gamma^2 + 0.044\gamma - 0.1535}$

for $\Delta\rho = \rho_s - |\rho_{SWNT}| \gg \Delta\rho_{SWNT} = |\rho_{SWNT}| - \rho_{SWNT,i}$ This difference is exploitable for length separation

The separation can be described mathematically either through a Flux (Nernst-Planck formulation) or in a single particle velocity sense. The difference in the scaling of the friction factor and the buoyancy force on the rod with aspect ratio results in the prediction that longer SWCNTs will travel with a greater velocity in response to an applied centripetal acceleration.

Length Separation by Centrifugation

Eqn 5 generates curves such as these

Distance per Day (mm / 24 h)

2 nm diameter
3 nm diameter
4 nm diameter
5 nm diameter
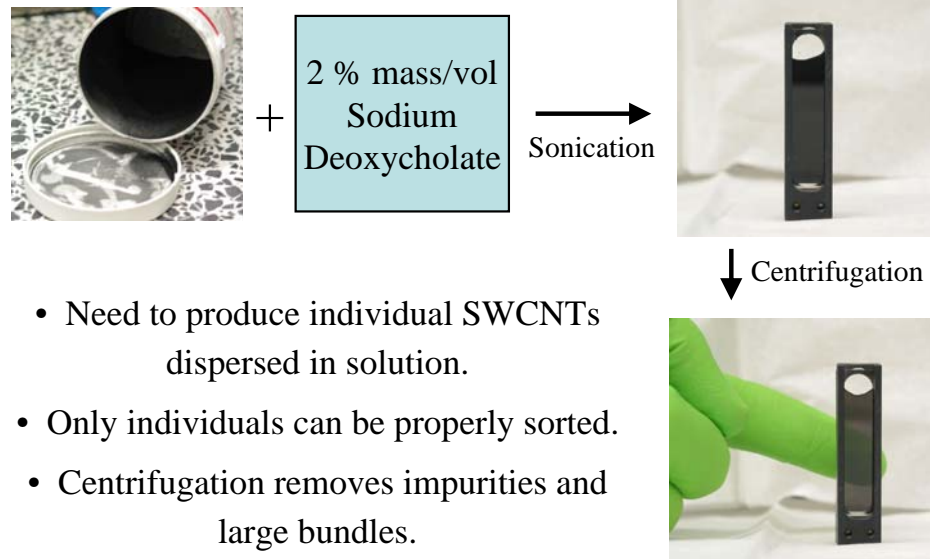6 nm diameter

Nanotube Length (nm)

A swinging bucket rotor is ideal for length separation.

Theoretical curves for the distance travel are approximately logarithmic with the length of the SWCNTs. A swinging bucket rotor is ideal for the separation as it limits the wall effects of the centrifuge tube.

Experimental Demonstration: Dispersion:

+

2 % mass/vol Sodium Deoxycholate

Sonication

Centrifugation

- Need to produce individual SWCNTs dispersed in solution.
- Only individuals can be properly sorted.
- Centrifugation removes impurities and large bundles.

The raw soot is intially dispersed via tip sonication (3 mm) in an ice bath with the deoxycholate or DNA surafactant resulting in the dark solution with 1 mg/mL of the raw soot in the solution. Centrifugation at 21 000 x g removes most of the non-SWCNT material, leaving a dark but more transparent dispersion, which is the parent solution used for the fractionation processes.
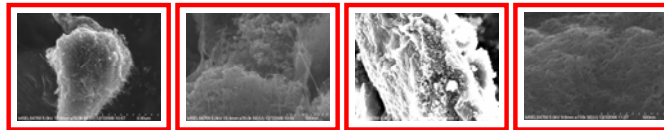
Purification in Dispersion
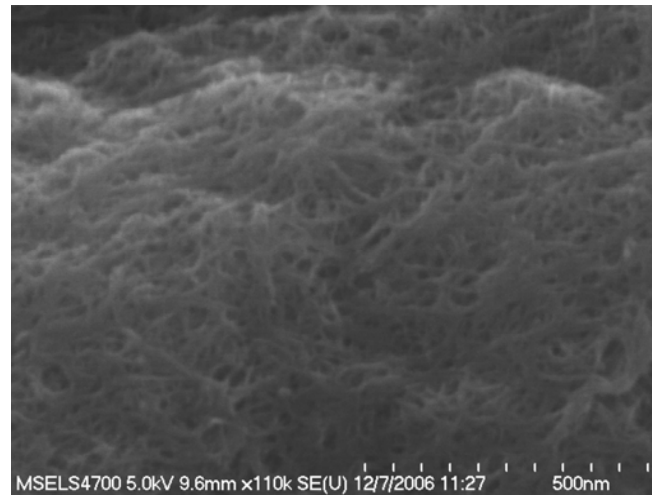
SEM images
by Thuy Chastek

Showing

CoMoCat starting material

Centrifugation bottoms

Supernatant SWNTs

MSELS4700 5.0kV 9.6mm ×110k SE(U) 12/7/2006 11:27   500nm

SEM images of the raw soot (first two), sediment from the initial centrifugation at 21 000 *g (3rd pict), and the supernatant from the initial centrifugation at 21 000 *g (last pict). The initial soot is measured to be (55 to 60) % SWCNTs by mass, by both TGA and UV-Vis-NIR absorption changes, and the supernatant approximately 90 % SWCNTs. The final image is certainly not indicative of a less than 10 % mass purity of SWCNTs that would be needed to explain the SEC results, or the less than 3 % purity which would be needed to explain the UC separation results.
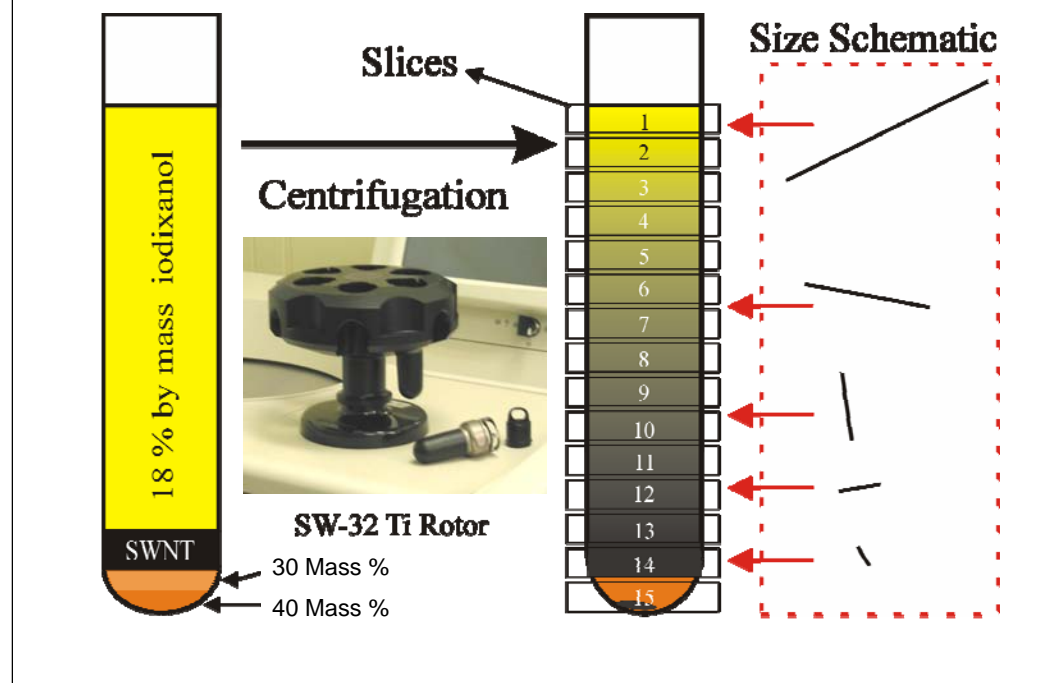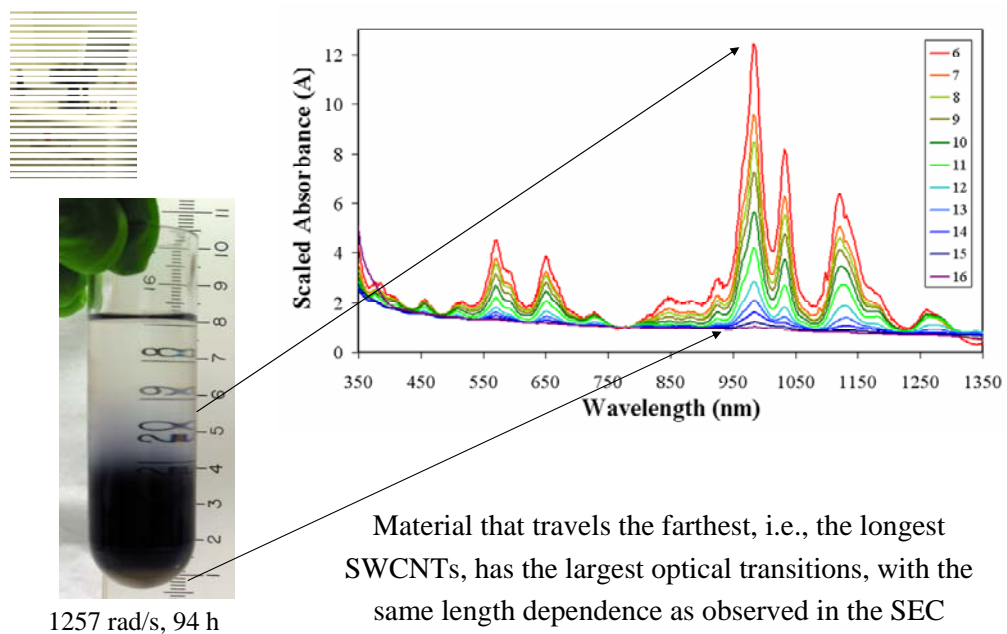
Schematic of the experiment, with the layer densities shown (SWCNTs are loaded in a 20 % iodixanol, all layers contain 2 % DOC), and the resulting distribution after separation.

Length Separation by Centrifugation

12 000 RPM (1257 rad/s),
94 h run time

← 1

← 16
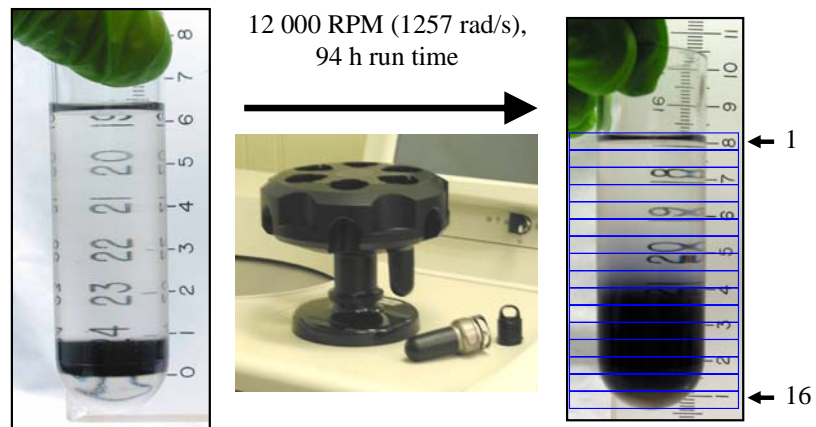
Pictures of an actual experiment, with the resulting distribution after separation shown, and the approximate location of the fractions. In this particular experiment approximately 0.7 mg of SWCNTs were in the pictured centrifuge tube.

Length Separation by Centrifugation

Material that travels the farthest, i.e., the longest SWCNTs, has the largest optical transitions, with the same length dependence as observed in the SEC

1257 rad/s, 94 h

Fractions collected after the 1257 rad/s, 94 h separation show substantial and monotonic increases in peak to baseline ratio, without evidence of chirality separation, with the distance travelled by the SWCNTs. Note the purplish color of the larger fractions due to the increase in relative size of the E22 features above the baseline absorption.

Length Separation by Centrifugation
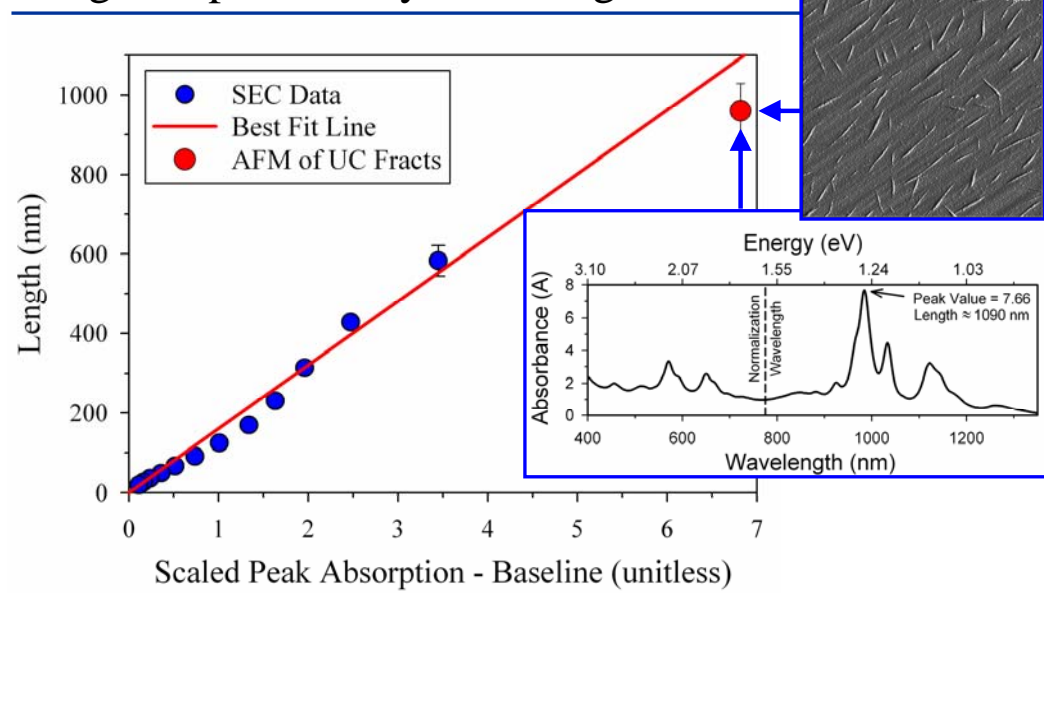
The easiest way to judge the length of the ultracentrifuge separated fractions is to scale using the UV-Vis-NIR results from the SEC. **FOR MY SPECIFIC SAMPLE AND ITS CHIRALITY DISTRIBUTION**, the best fit of length to the peak to baseline ratio is L = 160.4 nm * ((A(984 nm)/A(775 nm))-0.842). To test this function we have dialyzed several length fractions from the UC separation (and have been waiting on supplies to do more), and find that they fit the trend. Shown in red is the measured AFM length of an older (broader distribution) length fraction. The best fit projection is in good agreement with the measured value.
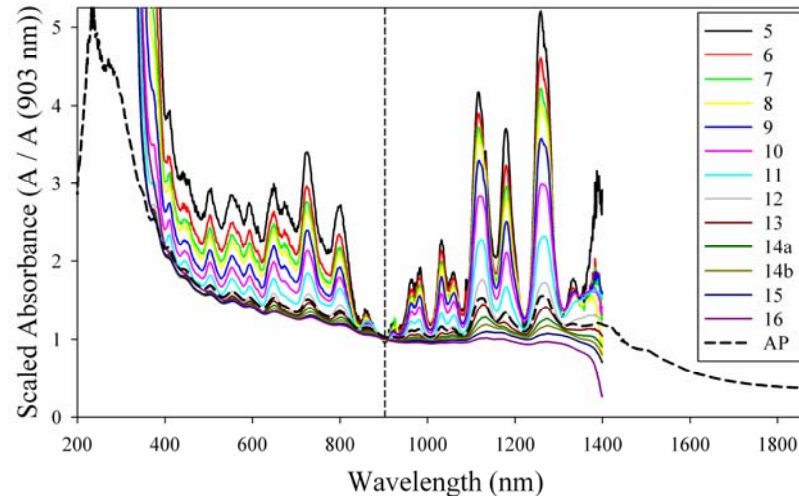
Length Separation by Centrifugation:

≈ 800 nm Avg. Length
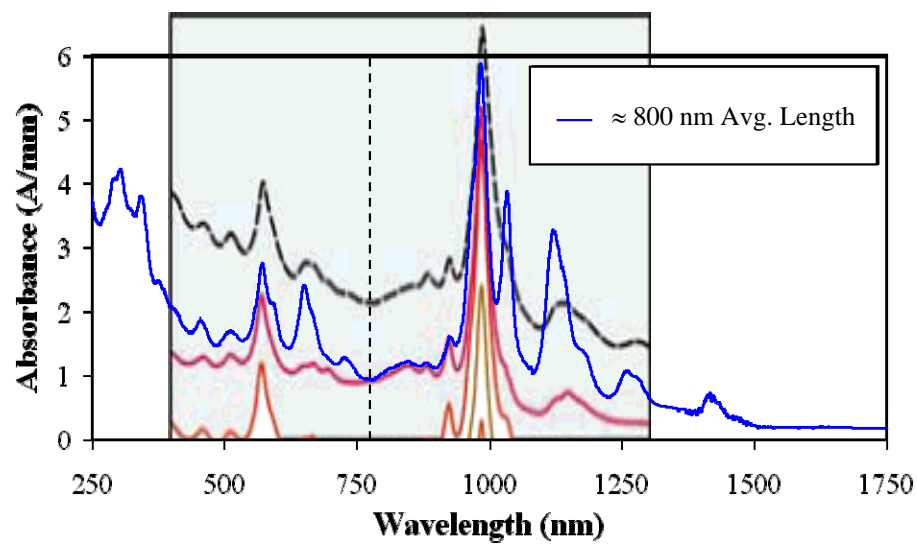
Chirality purified figure from Crochet *et al. J. Am. Chem. Soc.* **2007**

The increase in absorption is so significant that longer SWCNT solutions that are not chirality separated can have larger transition sizes than chirality sorted material. Shown is a comparison to spectra of heavily enriched (6,5) SWCNTs by Crochet *et al. J. Am. Chem. Soc.* **2007** (magenta line) to an chirality unpurified but approximately 800 nm long fraction (that has been dialyzed to remove the iodixanol). Note that the blue curve has a larger peak to baseline ratio at 984 nm, despite being composed of only approximately 20 % (6,5) SWCNTs.

Length Separation by Centrifugation:

An example of spectra from a HiPCO separation.
We have also separated EA and Laser type SWCNTs

As in the SEC, we also have run other sources of SWCNT material through the centrifugation separation. Above is a set of spectra from the separation of a HiPCO process sample. The unsorted solution is the dashed line. Deviation of the separated sample spectra below 400 nm and above 1300 nm are due to imperfect subtraction error of the (large) iodixanol solution absorption. Note that the size of the Pi-Plasmon peak is expected to be nearly constant across the fractions, indicating that several chirality features are approaching that size in the longest fractions. Also note that all of the chiralities are increasing at the same relative rate, this is not the effect of chirality separation.

Separation Parameter: Velocity

Initial → 785 rad/s 240 h | 1257 rad/s 94 h | 1570 rad/s 60 h | 3141 rad/s 15 h
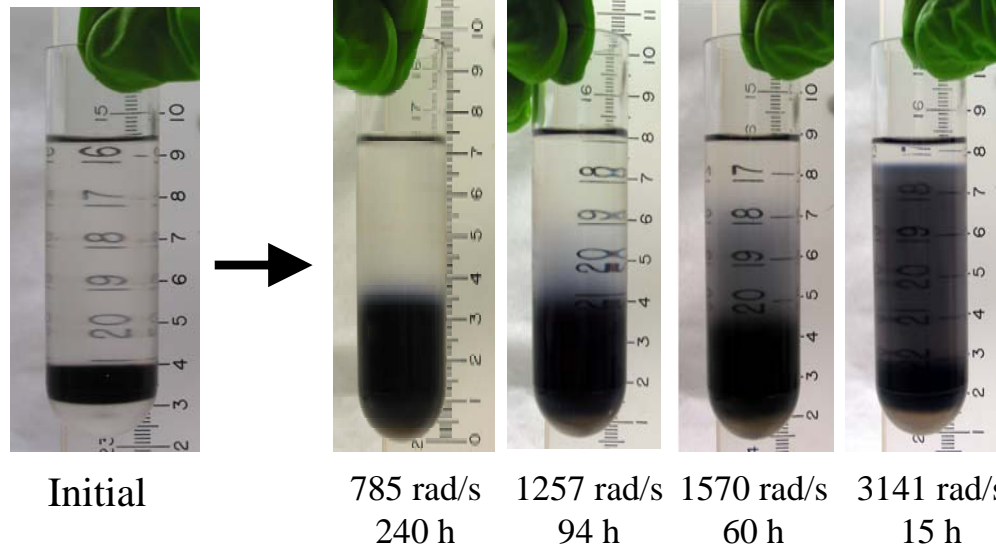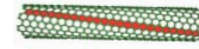
Identical integrated force in each experiment: Different results

This is not to say that everything is understood about the length separation in the UC. For instance here are shown pictures of the result from running the separation for identical total integrated force on the liquid, but with different rotational rates. Slower, longer separations proceed closely with the theoretical predictions. Faster separations seems to induce additional effects, such as potentially a sedimentation potential effect (due to redistribution of the density gradient polymer), which would align and cause electrophoretic of the motion of the SWCNTs and thus could conceivably generate the results of the 3141 rad/s separation.

Separation Parameter: Velocity
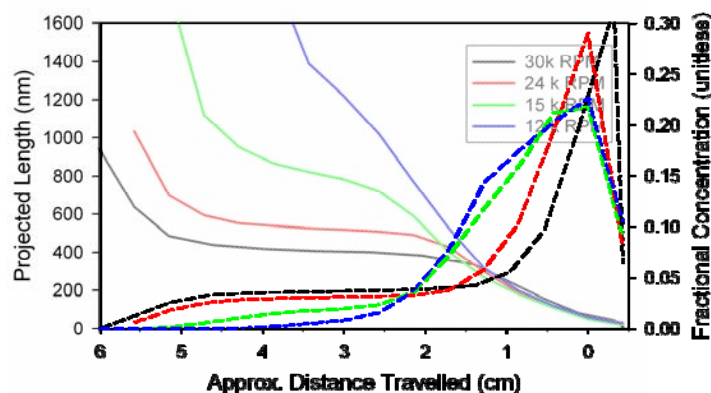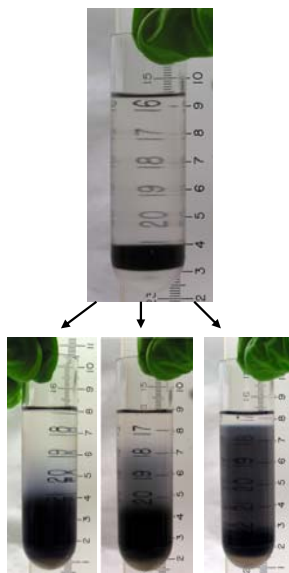
Integrated Avg. Length = 228 ± 5 nm

Using the UV-Vis-NIR length projection the length versus distance curves can be plotted. The 1257 rad/s separation most closely follows the theoretical form. Convincingly, normalization at 775 nm is demonstrated to be a good indicator of concentration by these curves. Integration of the length in each separation with the measured concentration in each fraction yields identical values for the average length of the initial identical injections. If the normalization were not a good indicator of concentration, then these curves would not reach equivalent summed values.

The curve for 1257 rad/s is consistent with a buoyant radius (using the equilibrium value for the nanotube plus micelle density) of ≈ 3.5 nm, combined with a towards the bottom of the tube directed drag due to the sedimentation of the density liquid polymer.
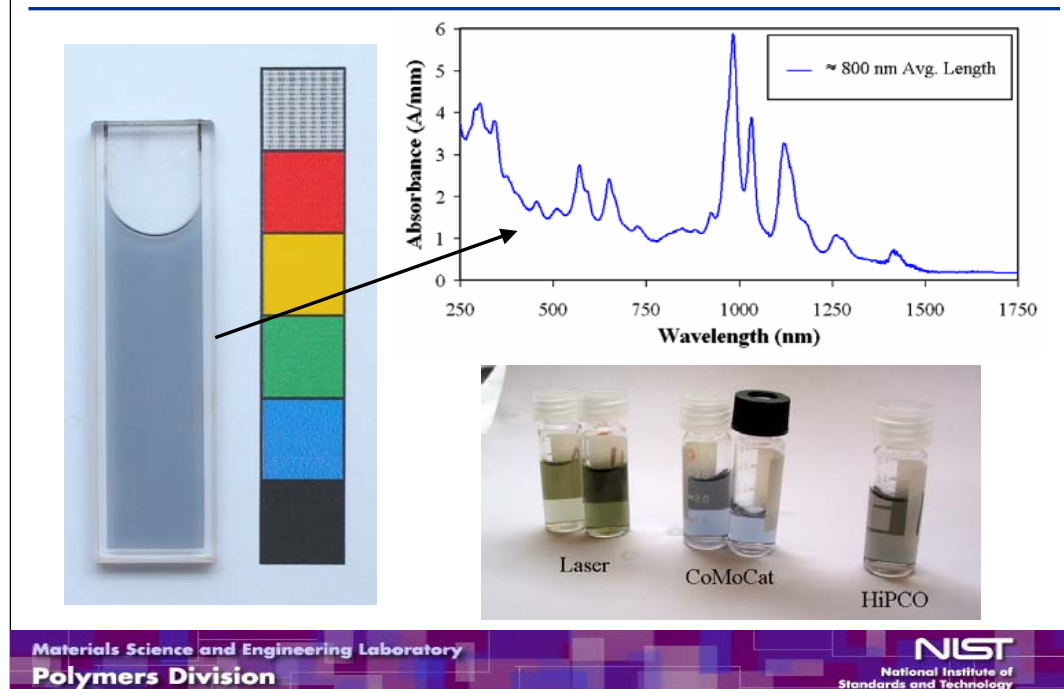
Picture of CoMoCAt solution color and spectra, and a picture of long SWCNTs from different material sources. Note that no chirality separation has been performed.

Conclusions:
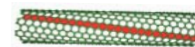
- Length is an important parameter for SWCNTs that can and should be accounted for.

- Separation improves the SWCNT optical properties.

- Multiple avenues for length separation exist that are compatible with other separations and future uses.

- Length and chirality purified materials will be increasingly available to the community.

Conclusions. The SEC work is available in Fagan et al. *JACS* **2007**, 129, 10607-10612.

Conclusion:

Laser CoMoCat HiPCO
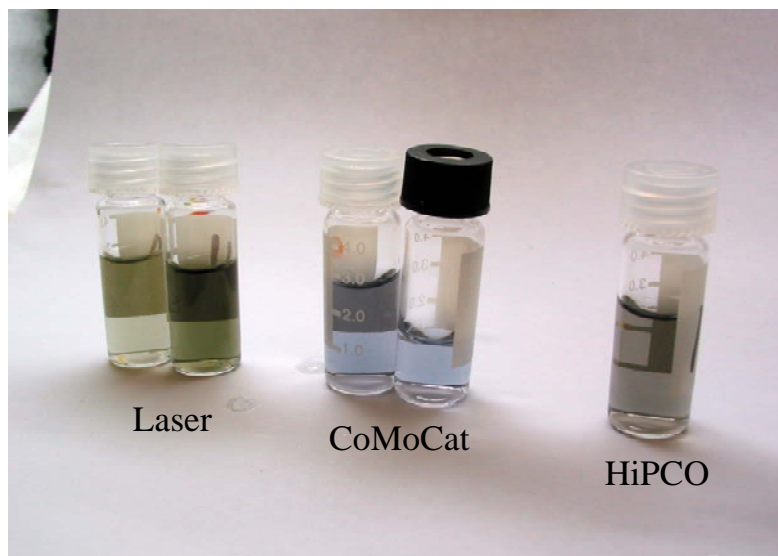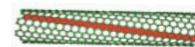
Materials Science and Engineering Laboratory
Polymers Division

NIST
National Institute of
Standards and Technology

Pictures of long SWCNTs from different material sources. Note that no chirality separation has been performed.